

Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) EP 0 917 208 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:  
19.05.1999: Bulletin 1999/20

(51) Int. Cl.<sup>6</sup>: H01L 31/0384, H01L 51/20,  
H01L 51/30, H01L 33/00

(21) Application number: 97203499.5

(22) Date of filing: 11.11.1997

(84) Designated Contracting States:  
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC  
NL PT SE  
Designated Extension States:  
AL LT LV MK RO SI

(72) Inventors:  
• Schropp, Rudolf Emmanuel Isidore  
3972 GE Driebergen (NL)  
• Salafsky, Joshua Samuel  
Rockford, IL 61114 (US)

(71) Applicant:  
Universiteit van Utrecht  
3584 CS Utrecht (NL)

(74) Representative:  
Land, Addick Adrianus Gosling  
Arnold & Siedsma,  
Advocaten en Octrooigemachtigden,  
Sweelinckplein 1  
2517 GK Den Haag (NL)

(54) Polymer-nanocrystal photo device and method for making the same

(57) Especially for reducing costs for photovoltaic cells, research is done all around the world for finding a solid state composition of creating an interpenetrating solid-state conducting material in a nanoporous network. Such device could also be used for LED (light emitting diodes), photo sensors, optical switches and even optical networks.

This invention relates to a photo device comprising a layer of nanometer sized particles and a conducting polymer in solid state, wherein the nanometer sized particles are chosen from the group of TiO<sub>2</sub>, ZnO, CdSe, CdS, ZrO<sub>2</sub>, SnO<sub>2</sub> and wherein the conducting polymer comprises PPV (polyparaphenylenevinylene) or a derivative thereof.

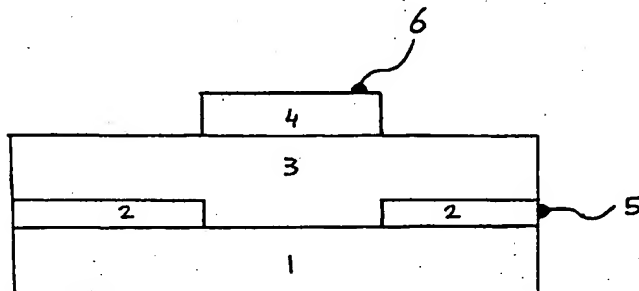


Figure 1

## Description

[0001] Especially for reducing costs for photovoltaic cells, research is done all around the world for finding a solid state composition of creating a interpenetrating solid-state conducting material in a nanoporous network. Such device could also be used for LED (light emitting diodes), photo sensors, optical switches and even optical networks.

[0002] This invention intends to offer a solution to the problem of creating an interpenetrating solid-state conducting material in a nanoporous network, for the purpose of creating stable, all-solid state photovoltaic cells. Thus, the instability problems associated with liquid-based electrolytes in nanoporous networks (1) can be eliminated. Prior methods have been published on the insertion of a polymer electrolyte into a preformed nanocrystalline  $\text{TiO}_2$  (titanium dioxide) network (2) but this methods have the disadvantage of being based on an ionic conductor thus limiting the device performance, rather than on an electronic conductor such as the one we describe here. Another prior method using conducting polymers (PPV and derivatives) replaces the inorganic nanocrystalline network with  $\text{C}_{60}$  and derivatives which act as electron-acceptors (3). However, in this method, the electron transport is restricted. Further,  $\text{C}_{60}$  is not a material which can be produced abundantly, and is thus expensive; it is also much less stable than inorganic materials. The present invention offers the stability, electron transporting properties, and low cost of a  $\text{TiO}_2$  interconnected network in combination with the hole-transporting, light-absorbing, stable properties of PPV (poly-paraphenylenevinylene). A further aspect of this invention is the ease of manufacturing, namely in a single thermal treatment of the inorganic and organic materials together.

[0003] An example of this method according to this invention uses a conducting polymer, p-PPV (precursor PPV) and a nanocrystalline material,  $\text{TiO}_2$ . A schematic cross-section of the cell is show, in Fig. 1. The polymer p-PPV was made by chemical synthesis (4).  $\text{TiO}_2$  nanocrystals were obtained from Degussa AG corporation, Germany. An approximately 0.7% methanol solution of the p-PPV was combined with a colloid of  $\text{TiO}_2$  made according to reference 5 to give a mixture of approximately 1:1 p-PPV and  $\text{TiO}_2$  by weight. This mixture was spin-coated on a glass substrate 1 with a transparent conducting coating 2, in this example  $\text{SnO}_2:\text{F}$ , to give a thin film 3. The film was heated to 320 °C for ten hours in vacuum and an aluminum contact 4 evaporated in such a way that there is no overlap with the transparent (with methods commonly known in the field), conducting coating on the glass on top of the film to complete the cell.

[0004] Current-voltage (IV) curves of the cells in the dark and in white light were measured at terminals 5 and 6 (Fig. 1) and a plot of this data is shown in Fig. 2 which demonstrates that the cells produce electric

power under illumination.

[0005] The main novelty and crucial distinction of this method over other methods is the thermal treatment step, which is necessary for both conversion of the p-PPV to its final conducting form, PPV; and, to produce electrical contact between the  $\text{TiO}_2$  particles to produce electron-carrying paths through the film. Our method is the first one to make operational photovoltaic cells of a conducting polymer, such as PPV, and a sintered electrically interconnected network of nanocrystalline particles, such as  $\text{TiO}_2$ . PPV has been shown to be a good hole-conducting material (4) and  $\text{TiO}_2$  an excellent electron transporter (1), so their combination together, prepared in a single thermal treatment step, also represents a significant advance.

[0006] The method is general for a range of temperatures, other polymers, or nanocrystals.

## Claims

1. A photo device comprising a layer of nanometer sized particles and a conducting polymer in solid state.
2. A photo device according to claim 1, wherein the nanometer sized particles are chosen from the group of  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{CdSe}$ ,  $\text{CdS}$ ,  $\text{ZrO}_2$ ,  $\text{SnO}_2$ .
3. A photo device according to claim 1 or 2, wherein the conducting polymer comprises PPV (polyparaphenylenevinylene) or a derivative thereof.
4. A photo device according to claim 1, 2 or 3, wherein the layer is a thin film of a photovoltaic cell.
5. A method for producing a photo device, according to claim 1, wherein the layer is heated to a predetermined temperature during a predetermined time.
6. A method according to claim 5, wherein the heating takes place at substantial underpressure or vacuum.

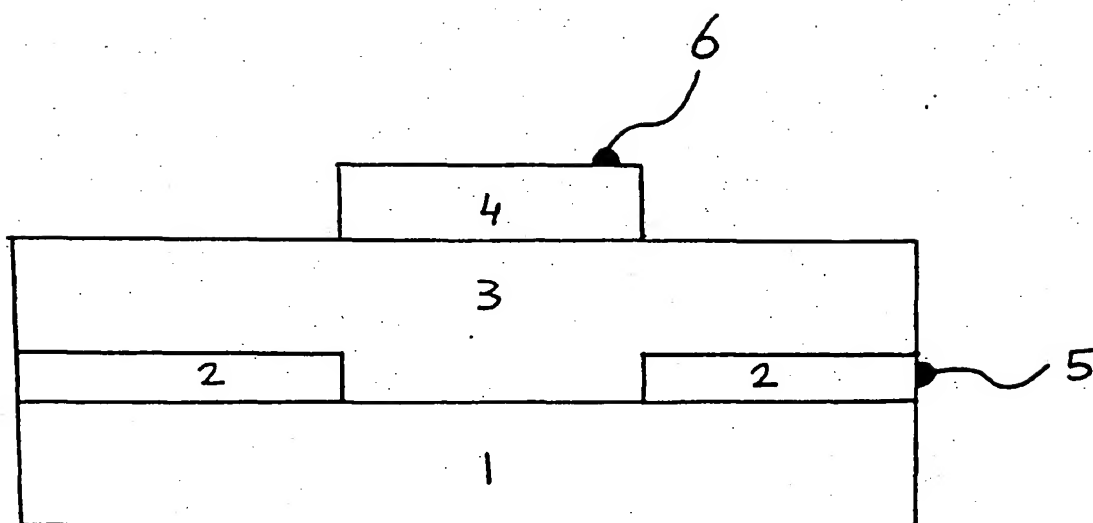


Figure 1

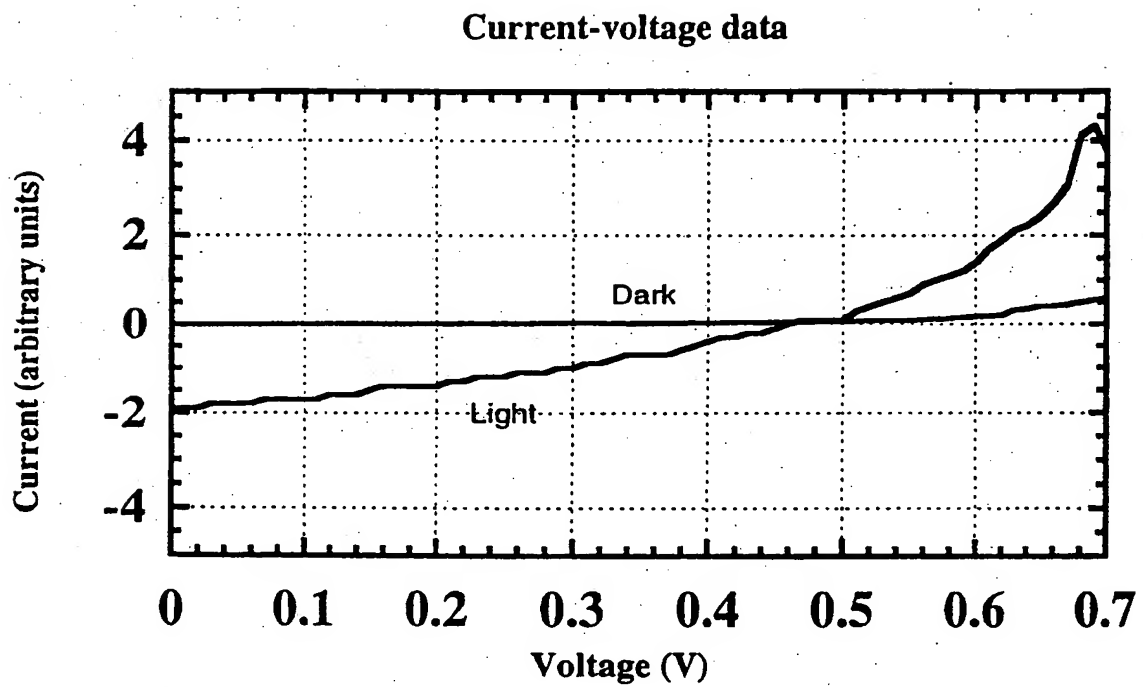


Figure 2



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 97 20 3499

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	N.C. GREENHAM ET AL.: "Charge separation and transport in conjugated-polymer/semiconductor-nanocrystal composites studied by photoluminescence quenching and photoconductivity" PHYSICAL REVIEW, B, CONDENSED MATTER., vol. 54, no. 24, 15 December 1996, NEW YORK US, pages 17628-17637, XP002060964 * page 17628 - page 17630 *	1-4	H01L31/0384 H01L51/20 H01L51/30 H01L33/00
X	N.C. GREENHAM ET AL.: "Charge separation and transport in conjugated polymer/cadmium selenide nanocrystal composites studied by photoluminescence quenching and photoconductivity" SYNTHETIC METALS, vol. 84, no. 1-3, 1 January 1997, AMSTERDAM, NL, pages 545-546, XP002060965 * the whole document *	1-3	
X	S.A. CARTER ET AL.: "Enhanced luminance in polymer composite light emitting devices" APPLIED PHYSICS LETTERS., vol. 71, no. 9, 1 September 1997, NEW YORK US, pages 1145-1147, XP000720223 * page 1145 *	1-3	H01L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 1 April 1998	Examiner Visentin, A
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 03.82 (p4/C01)



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 97 20 3499

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	KUCZKOWSKI A: "THE PROSPECTS FOR POLYESTER POLYMER-CDS POWER COMPOSITES IN PHOTOELECTRONIC DEVICE APPLICATIONS" JOURNAL OF PHYSICS D. APPLIED PHYSICS, vol. 22, no. 11, 14 November 1989, BRISTOL, GB, pages 1731-1735, XP000072966 * the whole document * -----	1-6	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>1 April 1998</b>	Examiner <b>Visentin, A</b>
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons  &amp; : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03/92 (P4/C01)